Indian J. Phys. **72B** (6), 615-622 (1998)

IJP B
an international journal

Surface enhanced Raman spectroscopic study of poly (*o*-methoxy aniline) organised in Langmuir-Blodgett film

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Received 31 August 1998, accepted 9 September 1998

Abstract : Poly *o*-methoxyaniline (POMA) has been successfully organized in LB films. UV-Vis absorption spectroscopy shows that *as*-prepared LB film is partially protonated and can be easily deprotonated and reprotonated by alkali and acid treatment respectively. Normal Raman spectrum (NRS), surface enhanced Raman spectrum (SERS) of POMA in LB film on silver islands and tentative assignment of the relevant Raman bands for POMA characterisation are reported. Three orders of magnitude enhancement in Raman intensity has been observed in SERS compared to that in NRS. Layer effect study showed maximum enhancement in a two-layered LB film suggesting the presence of voids in the monolayer film. Surface plasmon resonance is found to be the dominant factor for enhancement. SERS study reveals that in the LB film the organisation of POMA is such that the quinoid ring is out of the plane and the benzoid ring is in the plane of the film surface.

Keywords . Polyaniline, Langmuir-Blodgett film, Raman spectroscopy

PACS Nos. 33.20.Fb, 33.20.Tp

1. Introduction

During recent years polyaniline and its derivatives have attracted a lot of attention as these materials are extremely stable in air as well as in water and their electrical conductivity can be regulated over a wide range [1,2]. Polyanilines have also found uses in electrochromic display, ion exchangers and also in various microelectronic and other devices [3-6]. In spite of a large number of publications, polyaniline is still studied with interest as the nature of conduction in various conducting forms are not yet resolved and also the fabrication of good quality ultra thin stable film for device application has not yet been standardised. The use of the LB technique to deposit ultra thin anisotropic conducting polymer films exhibits great promise in microelectronics and molecular electronics as the molecular architecture and superstructure of suitably modified polymers in such films can be controlled to achieve the desired network for the device application.

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Although extensive Raman scattering studies of polyaniline have been reported [7-12], little is known about the surface enhancement of Raman scattering of this polymer. With the vibrational information available from this technique, the molecular forms and the orientation of adsorbed species on the metal surfaces can be investigated. Surface enhanced Raman spectroscopy (SERS) is an useful technique for studying the nature of physical and chemical adsorption of molecules on metals. Several factors [13] are reported to influence the enhancement of Raman signals of molecules adsorbed on the metal surface. The enhancement factor depends on the excitation wavelength, metal surface, surface microstructure and the electronic structure of the adsorbates. If the exciting radiation frequency coincides with the surface plasmon resonance frequency of the metal, maximum enhancement is observed. This is termed as the electromagnetic effect [14]. The other effect that may contribute to the enhancement is charge transfer between the adsorbate and the metal which modulate the Raman scattering polarizability through molecular vibration. [15, 16]

In an earlier communication [17] we have reported the electrical conductivity study of POMA organised in Langmuir Blodgett films. Conductivity anisotropy has been found in the LB film In this paper we report the NRS and SERS study of POMA organised on Ag-island film by Langmuir-Blodgett technique. Characterization of LB film by UV-Vis absorption spectroscopy is also reported.

2. Experimental

The synthesis of poly *o*-methoxyaniline (POMA) has been reported by Mattoso and Faria's group [18]. Molecular structure of protonated and deprotonated POMA are shown in Figure 1 Using similar method protonated POMA (green coloured) of higher weight fraction (molecular weight ≈ 28000) was synthesized using chemical oxidation with ammonium persulfate Details of the synthesis has been reported elsewhere. [18]

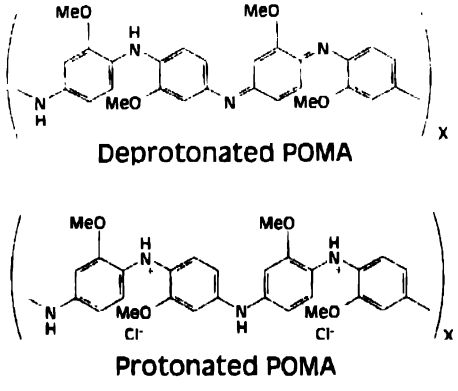

Figure 1. Schematic representation of (a) deprotonated blue form of poly (*o*-methoxy aniline (b) protonated green form of poly (*o*-methoxy aniline salt) after doping.

Freshly prepared protonated POMA solution dissolved in 50% mixed solvent of N-methyl pyrrolidone (NMP) and benzene was spread onto neutral (pH = 6.8) water subphase to form monolayer. When left on the water subphase at a constant pressure *i.e.* 15 mN/m, monolayer was found to be fairly stable with less than 10% area loss over an hour. The pressure-area (π-A) isotherm was recorded under a barrier compression rate of 5 cm^2 min^{-1}. The monolayer was compressed to a pressure of 25 mN m^{-1} and then lifted on a fluorescence grade glass and/

or quartz substrate by Y-type of deposition. The substrate dipping speed was maintained at 5 mm min^{-1} with a drying time of 20 min after each lift. Transfer ratio of 0.9 was obtained during deposition.

According to the method described elsewhere [19] silver Island films of 50 Å mass thickness were prepared by slow vacuum evaporation (0.1–0.2 nm/s) of the metal under a pressure < 10^{-5} Pa onto warm glass substrates kept at 200°C. The thickness was monitored with a quartz crystal oscillator (model DTM-101, Hi-tech Instruments Pvt. Ltd., India). The control of the substrate temperature during deposition permitted the growth of a film with a highly homogeneous distribution of particle shape. Island diameter as obtained from Scanning Electron Micrograph (Hitachi S-415A) was 60-100 Å. The plasmon absorption of the Ag film was broad and centered at 450 nm.

Raman spectra were recorded by a Spex (model 1403) double monochromator. A Spectra Physics argon ion laser (model 2020-5) was used for Raman excitation. Laser power was always maintained below 20 mW for excitation. The spectral band pass was 2 cm^{-1}. A Spex Datamate 1B was used for spectrometer control, data acquisition and analysis. Absorption spectra were recorded on Shimadzu 2010 PC UV-VIS spectrophotometer.

3. Results and discussion

3.1 POMA-LB film preparation :

Figure 2 shows the pressure-area isotherm of POMA. Monolayer shows solid condensed phase at higher pressure. The molecular weight (obtained from gel permeation chromatography) of POMA used is 28000 and formula weight of the repetitive unit of the polymer is about 500. Using these values the pressure-area isotherm shows the area per repetitive unit in the condensed phase is about 20 Å which is similar to the results obtained by others [18, 20].

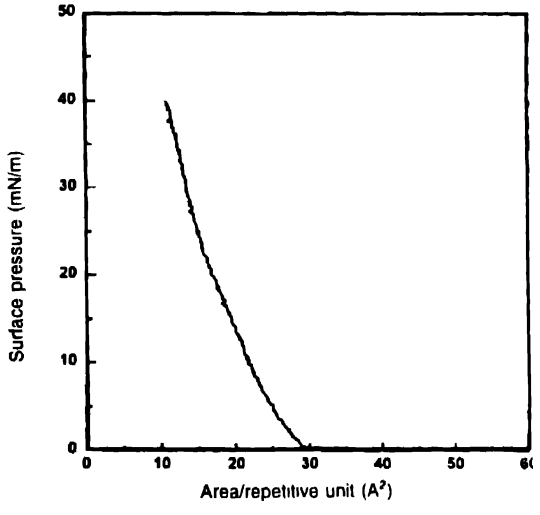

Figure 2 Surface pressure-area/repetitive unit (II-A isotherm) plot for poly (*o*-methoxyaniline) monolayer on water subphase at 25°C.

LB film of POMA is deposited on quartz substrate. Figure 3 shows the UV-Vis absorption spectra of 16 layer LB film under different experimental conditions. In *as*-prepared LB film a

broad band with peak at 630 nm is observed. To know the extent of protonation of the *as*-prepared LB film we deprotonated and protonated the film by base (0.1 M NH_4OH) and acid (1.0 M HCl) treatment respectively. Fully deprotonated LB film shows broad absorption peak at about 540 nm. Due to protonation this peak shifts towards lower energy and its intensity decreases. After sufficient acid treatment this peak almost disappears and the colour of the film becomes green (protonated form). Similar type of bathochromic shift and decrease in intensity is observed for electrochemical protonation of polyaniline [21, 22]. The results demonstrate that the extent of protonation decreases during monolayer formation at neutral water subphase.

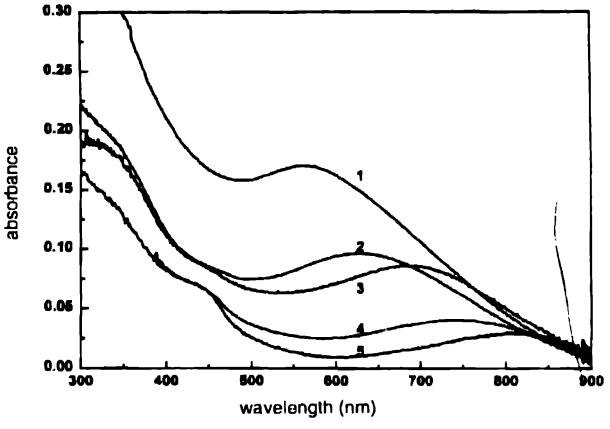

Figure 3 UV-Vis absorption spectrum of 16 layered LB film of POMA under different experimental condition 1- Alkali treated (0.1M NH_4OH) LB film, 2- *As*-prepared LB film 3- 5- HCl vapour exposed LB film exposed for 5 minutes, 1 hour & 24 hours respectively

3.2 Normal Raman and surface enhanced Raman spectroscopic study :

NRS and SERS of *as*-prepared POMA-LB film are recorded in the wavenumber range 1200-1800 cm^{-1}. Though our excitation wavelength range (450-520 nm) is in the trough region of the absorption spectrum (Figure 3 curve 2) the finite absorbance in this region may give pre-resonance Raman Spectrum. Stretching modes of the 'repeat unit' generally appear in this range. This range is necessary and sufficient for 'semi-quantitative' utilisation of the spectra for POMA characterization. Figure 4 shows the NRS and SERS spectra of POMA-LB film. For NRS twentyfive monolayers on glass substrate and for SERS single monolayer film are used To know the relative enhancement factor both NRS and SERS are measured under identical experimental condition and Raman intensity scale is calibrated in terms of count/layer/watt/scan. Figure 4 shows broad and overlapped multiple Raman bands. This type of broad, overlapped Raman band is quite common for polyaniline film [10]. Indeed in this spectral range organic monolayer often shows fairly intense broad background attributed to the formation of surface carbon on intense laser radiation. [23] We rule out this possibility in our SER spectrum as the laser excitation power (20 mW) has been kept low. Using Microcal ORIGIN 4.1. program the spectral peak fitting has been obtained. We have used Gaussian distribution for the Raman band. [24] Deconvoluted bands are also shown in Figure 4. Table 1 shows the NRS and SERS data with relative enhancement factor and tentative assignments. The vibrational frequencies agree with that reported in the literature. [7-9]

Table 1. Raman and SER spectra data for POMA Langmuir-Blodgett film

NRS (cm^{-1})	SERS (cm^{-1})	Enhancement factor	Assignment
1645			benzoid ring stretching
1605	1595	6.4×10^2	quinoid ring stretching
1548			
1495	1515	2.9×10^2	C= N stretching
1446	1449	5.6×10^2	
1395			N = N stretching
1345	1367	3.4×10^2	-C-N$^+$- stretching
	1292		C-N stretching

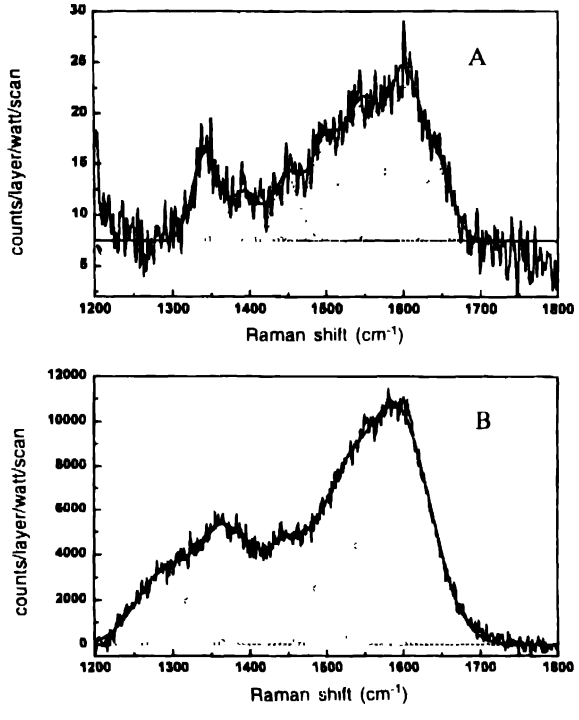

Figure 4 A) Raman spectrum of 25 layered POMA LB film B) SER spectrum of a monolayered LB film of POMA on silver islands Broad and overlapped Raman peaks are deconvoluted by spectral peak fit Deconvoluted peaks are shown by dotted lines Raman intensity is calibrated in terms of counts/layer/watt/scan

In SERS all the bands are enhanced by 2-3 order of magnitude except 1645, 1548 and 1395 cm^{-1} bands. The 1645 cm^{-1} benzoid ring stretching mode almost disappear in the SERS spectrum whereas at $\approx$ 1600 cm^{-1} (1605 cm^{-1} in NRS and 1595 cm^{-1} in SERS) is enhanced significantly. This according to surface selection rule, indicates that the quinoid ring is out of

the plane and the benzoid ring is in the plane of LB film surface. [25] The peak at ≈ 1500 cm^{-1} (1495 cm^{-1} in NRS and 1515 cm^{-1} in SERS) is assigned to the stretching vibration of C=N groups and indicates the presence of imine sites.

Another very interesting feature is the observation of a weak but distinct peak at 1395 cm^{-1} in the NRS of multilayered LB film. This band is absent in SERS of monolayered LB film. This band is not generally described in the literature, and possibly corresponds to the – N=N- mode which is not normally present in the *as*-polymerised film. In multilayered film - N=N- coupling may be possible between the two adjacent layers due to laser excitation. [26] This peak is absent in the SERS of the monolayer film where such linkage is unlikely.

The peak at ≈ 1350 cm^{-1} assigned as -C-N^{+}- stretching corresponds to the presence of polaron. [10] This band is absent in the completely deprotonated state (alkali treated). Intensity of this band increases with the increase of protonation. [27] The absorption spectrum of *as*-prepared POMA LB film shows that the film is partly protonated and the appearance of the 1350 cm^{-1} band in the LB film is reasonable.

Figure 5 shows the layer effect on SERS intensity. Maximum enhancement is observed in the two layered-LB film This indicates that the short ranged surface plasmon resonance is dominant. If the short ranged interaction play the dominant role, monolayer should show maximum enhancement. Observation of maximum enhancement in two layered film rather than in a monolayered film indicates that during the fabrication of monolayer some voids are generated which are subsequently filled up by the second layer. Additional layers have insignificant effect on SERS. Multiple layers are known to give bulk properties and Normal Raman Spectrum is obtained.

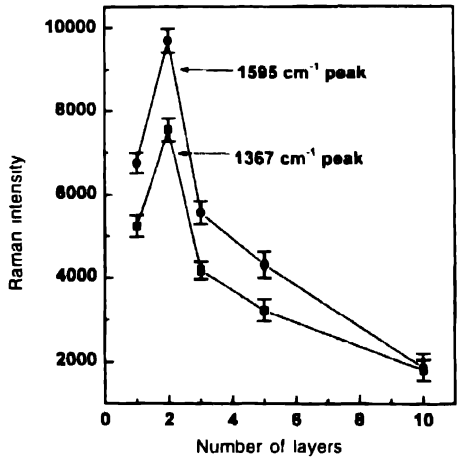

Figure 5. Variation of SER intensity with number of layers of POMA in LB film

Figure 6 shows the Raman excitation profile of 1595 cm^{-1} mode. With increasing excitation energy intensity of the 1595 cm^{-1} mode increases. This may arise due to resonance of the Raman band or due to surface plasmon resonance [14]. By close monitoring of the absorption spectrum of *as*-prepared LB film (Figure 3) the change in absorbance in the range of excitation wavelength is negligible. Comparing with the absorption spectrum of Ag-island film where the

change in absorbance is sharp we can say that the enhancement of 1595 cm^{-1} mode is surface plasmon resonance dominated.

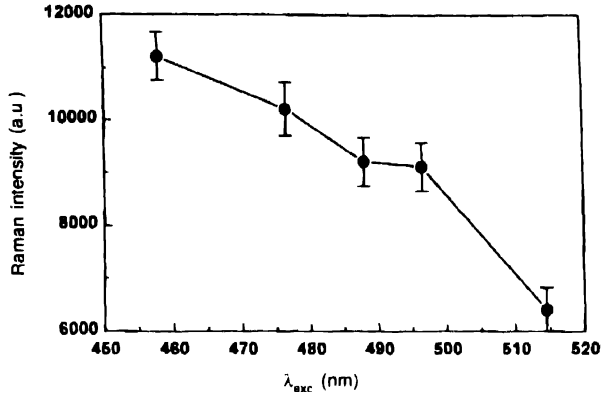

Figure 6 SERS excitation profile of 1595 cm^{-1} Raman band of POMA in LB film

4. Conclusion

High molecular weight protonated POMA forms stable monolayer at air-water interface and can easily be transferred onto glass/quartz substrates.

Absorption spectroscopic study shows that *as*-prepared LB film is partly protonated. Deprotonation and protonation of this LB film can easily be done by alkali and acid treatment respectively.

About three orders magnitude enhancement in Raman intensity is observed in SERS compared to NRS. Maximum enhancement is observed in two layered LB film. This indicates that the surface plasmon resonance is dominant for SERS activity. Raman excitation profile of the quinoid ring stretching mode also confirms short range interaction. The presence of -C-N^+- stretching mode confirms the protonated state of POMA in the LB film SERS study indicates that in the LB film quinoid ring of POMA is out of the plane and the benzoid ring is in the plane of the film surface.

5. Acknowledgment

The authors express their thanks to Department of Science & Technology, Government of India for financial support. One of the authors (P.P.) acknowledges the CSIR Pool scheme of the Government of India. Joydeep Chowdhury likes to thank Dr. Manash Ghosh of Spectroscopy Department, IACS for useful discussions

References

[1] E M Genies, P Hany and C J Jantier *Appl Electrochem* **18** 751 (1988)

[2] J P Travers, J Chroboczek, F Devreux, F Genoud, M Nechtschein, A Syed, E M Genies and C Tsintavis *Mol. Cryst Liq. Cryst.* **121** 195 (1985)

[3] T Matsunga, H Raifuker, T Nakajima and T Kawagoe *Poly Adv. Technol* **1** 33 (1990)

[4] G Gustafsson, Y Cao, G M Treacy, F Kalvettey, N Colaneri and A J Hegger *Nature* **357** 277 (1992)

[5] J J Langer *Mater. Sci* **14** 41 (1988)

[6] M Leclere, J Guay and L H Dao *Macromolecules* **22** 649 (1989)

[7] T Hagiwaga, T Demura and K Iwata *Synth. Met* **18** 317 (1987)

[8] J Tanaka, N Mashihita, K Mizoguchi and K Ume *Synth. Met* **29** E175 (1989)

[9] M Tsuboi *Spectrochim. Acta.* **16** 505 (1960)

[10] A Hugot-Le Goff and M C Bernard *Synth Met* **60** 115 (1993)

[11] T Fukuda, H Takezoe, K Ishikawa and A Fukuda *Synth Met.* **69** 175 (1993)

[12] M C Bernard and A Hugot-Le Goff *Synth. Met.* **85** 1145 (1997)

[13] A Otto in *Light Scattering in Solids* ed M. Cardona and G Guntherodt (Berlin : Springer) **Vol. 4** (1984)

14] D S Wang and M Kerker *Phys. Rev.* **B24** 177 (1992)

[15] D P Dilella and M Moskovits *J Phys. Chem* **85** 2042 (1982)

[16] H Abe, K Manzel, W Schulze, M Moskovits and D P Dilella *J. Chem Phys* **74** 792 (1981)

[17] A Pal, D Talukdar and T N Misra *Solid State Commun* **99** 633 (1996)

[18] R M Faria, L H C Mattaso, M Ferreira, O N Oliveria Jr, D Goncalves and L O S Bulhoes *Thin Solid Films* **221** 5 (1992)

[19] U Guhathakurta-Ghosh and R Aroca *J Phys Chem* **93** 6125 (1989)

[20] M Ando, Y Watanabe, T Iyoda, K Honda and T Shimidzu *Thin Solid Films* **179** 225 (1989)

[21] Y Furukawa, T Hara, Y Hyodo and I Harada *Synth Met* **16** 189 (1986)

[22] M McManus, S C Yang and R J Cushman *J Chem Soc Chem Commun* 1556 (1985)

[23] A Otto *Surf Sci* **75L** 392 (1983)

[24] M C Tobin in *Laser Raman Spectroscopy Chemical Analysis a Series of Monography of Analytical Chemistry and its Application* eds P J Elving and I M Kolthoff (New York Wiley Interscience) p66 (1970)

[25] J A Creighton *Surf Sci* **173** 665 (1986)

[26] N Kumar, F Ginder, G Bouyssoux and A Sartre *Synth Met* **36** 111 (1990)

[27] M C Bernard, S Codoba-Torresi and A Hugot Le Goff *Solar Energy Materials and Solar Cells* **25** 225 (1992)